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COMPLETE SPECIFICATION.

Improvements in or relating to Preparations of Modified Products of Galactomannans, Polyuronic Acids and Galactans.

We, ALFRED HEINRICH BLATTMANN; HANS HEINRICH BLATTMANN-BERGER; MARGUERITE HEDWIG TESDORPF-BLATTMANN; trading as Blattmann & Co., all of Swiss Nationality, of Wädenswil, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of degradation products and other modified products of mucilaginous natural substances of high molecular weight belonging to the group consisting of galactomannans, polyuronic acids and galactans. It relates also to improved derivatives and/or degradation products prepared by the process.

According to the process hitherto known, the degradation of galactomannans, polyuronic acids and galactans is carried out in aqueous suspensions or by a roasting process in open pans or by mechanical degradation. These processes have important disadvantages among which are:

In the degradation of such substances in aqueous suspension additional working steps are necessary for the dispersion of pulverulent, dry starting materials in the liquid media and for the isolation and drying of the derivatives, and there is a considerable loss of water soluble portions of the products in the liquid. Therefore, degradation in suspension can be used to a limited extent only and is expensive. The roasting process in open pans tends to burn the raw material, causing the formation of non-uniform products, and due to the presence of atmospheric oxygen in the roasting process discolourations occur and dark coloured degrad-

ation products are obtained. Moreover, when pulverulent organic substances are roasted at the higher degradation temperatures in the presence of oxygen, there is great danger of explosions. Mechanical degradation, e.g. by means of ball mills, is time-consuming and rather limited in its usefulness, being effective only to bring about slight degrees of degradation.

An important object of the present invention is to provide a process by which the above mentioned disadvantages can be overcome.

It is another important object of the invention to provide new and improved thermal modification products of galactomannans, polyuronic acids and galactans, which are useful for purposes not served by known products of the thermal modification or degradation of such substances.

According to the present invention, there is provided a process for producing modification products of a natural substance of high molecular weight selected from the group consisting of galactomannans, polyuronic acids and galactans and mixtures thereof or with other thermally degradable carbohydrate materials which comprises dehydrating a finely divided mass of said substance in its native form, or in a pretreated or in partially degraded form, if desired in presence of a reactant capable of degrading or forming a derivative with said substance, under vacuum at increasing temperatures insufficient to cause pasting in the mass, then while excluding oxygen from the mass treating it thermally or thermally and chemically until a desired degree of modification is attained, and then cooling the mass while excluding oxygen from it.

The thermal or thermal and chemical treat-

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ment and the fluid cooling may be effected in a reducing atmosphere.

The starting materials that can be modified advantageously according to the invention include galactomannans, such as carob or locust bean gum and guar, polyuronic acids, such as tragacanth, gum arabic, pectins, algin or carageenin and galactans, such as agar-agar, and also mixtures of these substances one with another or with other thermally degradable carbohydrate materials. The starting materials can be used in native, pre-treated, or partially degraded condition, provided that they are in a dry to moist pulverulent form. Among the pretreatments which can be applied to them are a mechanical treatment, e.g. by fine grinding, a chemical treatment, e.g. with SO_2 , a biochemical treatment, e.g. by enzymes, or any desired combination of these.

Among the reactants which can be used are the following which serve to accelerate or enhance the thermal degradation of the mucilaginous substance: organic or inorganic acids, such as, for example, hydrochloric acid, nitric acid, phosphoric acid, formic acid, acetic acid, oxalic acid and others; and inorganic and/or organic salts, such as, for example, ammonium chloride, sodium hydrogen sulfate, aluminium chloride, aluminium sulphate, calcium chloride, sodium oxalate, sodium phthalate, and other alkali and alkaline-earth salts.

The process can also be carried out to advantage by the use of reactants which enter into chemical combination with the finely divided mucilaginous substance or with its dehydration or degradation products, for the preparation of derivatives by reactions such as, for example, etherification with e.g. ethylene oxide, propylene oxide, or monochloroacetic acid, esterification, acetal-formation with e.g. formaldehyde, polyoxymethylene, acetaldehyde, or dialdehyde such as glyoxal, or nitrogenization with ammonia, urea, trimethylamine, hydrazine, triethylanolamine, or other reactive nitrogen or amino compounds.

The water content of the dry to moist pulverulent starting material can vary within wide limits, the process being applicable to predried products which contain less than the commercial free water content as well as to so-called moist materials such as are discharged in crumbly form from filter presses, or suction filters in the course of manufacture.

The dehydration of the mucilaginous material under vacuum can be continued, at temperatures increasing into the range of 90 to 110°C, until the material practically contains no more free water, i.e., is substantially completely anhydrous, or only until it is so dehydrated that in the ensuing thermal treatment no gel-formation or lump formation

can take place. In general the dehydrated material contains so little moisture that practically no moisture will evaporate from it in the course of the ensuing thermal treatment, at increasing temperatures in the range of 130 to 180°C, and cooling.

The thermal treatment and the cooling, each with the exclusion of oxygen, then can be carried out under subatmospheric, normal, or a superatmospheric pressure. When carried out in a non-oxidizing gaseous atmosphere, nitrogen, carbon dioxide, gaseous SO_2 , or other gases inert to the material can be used. When desired, the pH of the material can be adjusted to a desired value prior to the cooling by the addition of a suitable neutralizing medium, e.g. ammonia.

In order to obtain an homogeneous product, the process is preferably carried out in autoclaves provided with suitable devices for continuously stirring the reaction material and for adjusting the heating temperature.

By means of the present invention, finely divided galactomannans, polyuronic acids and galactans are converted into extraordinarily valuable degradation products and derivatives, and the operations are carried out under most advantageous conditions. Being performed under vacuum and/or with the exclusion of oxygen, the process is explosion-proof. The products which result, in comparison with products obtained according to the hitherto known processes, are brighter in colour and more uniform in quality and in the degree of conversion; they have a smaller content of oxidized matter and better film-forming characteristics; and they can be prepared with degradation to any desired degree of viscosity. Because the substances treated retain their reactive OH-groups, derivatives can be obtained from them which show more uniform substitutions and are distinguished by higher solubilities and more flexible film characteristics than in the case of known derivatives of like substances. By virtue of these improvements the products obtained according to this invention are especially suitable for impregnating paper and for the surface sizing of paper, as well as for finishing, sizing and film printing in the processing of textiles.

The practice of the invention will be further understood from the following illustrative examples.

EXAMPLE 1:

200 kg of guar flour of commercial dryness (e.g., 15% H_2O) and in native condition is impregnated under vacuum of approximately 30 mm mercury with 405 grams of HCl gas and, while maintaining the vacuum at approximately 60 mm of mercury, the mass is brought gradually within 3 hours to 97°C with continuous removal of water, whereupon the temperature is increased to

110°C. Then the vacuum is destroyed by admission of nitrogen and the temperature is maintained at 110°C until a desired degree of modification is attained, whereupon the mass is cooled to ambient temperature in the nitrogen atmosphere.

EXAMPLE 2:

175 kg of caruba flour in native condition is sprayed with 750 cm³ of concentrated (36%) hydrochloric acid and then subjected to vacuum of approximately 100 mm mercury while being stirred in an autoclave. Subsequently with continuous removal of water, while maintaining the vacuum, the temperature is increased to 95°C within 2½ hours. Then the material is heated under continuing vacuum to 130°C and maintained at this temperature, for example, for approximately 3½ hours, until the desired degree of conversion is attained, whereupon the mass is cooled under vacuum.

EXAMPLE 3:

175 kg of commercially dry guar flour pre-treated by fine grinding is mixed with 175 kg of degraded, pulverulent potato starch (thin boiling or oxidized starch). The mixture is subjected to vacuum of approximately 30 mm mercury in an autoclave provided with a stirrer and acidified with 650 grams of HCl gas. Then the mixture is brought gradually to 98°C while maintaining a vacuum of approximately 60 mm mercury and continuously removing water, whereupon the temperature is increased to 160°C. Then the vacuum is replaced by CO₂ gas which is introduced into the autoclave to a pressure of 1.5 atmospheres, and heating at 160°C is continued, for example, for approximately 2 hours, until a desired degree of modification is attained. The material is then cooled in the CO₂ atmosphere.

EXAMPLE 4:

100 kg of guar powder in commercially dry native condition is acidified with 175 g of HCl gas under vacuum. While maintaining the vacuum, the mass is heated with continuous removal of water until within 3½ hours the temperature reaches 107°C, whereupon the temperature is raised to 130°C. Then the material is kept under vacuum and at 130°C for 1½ hours, whereby the desired modification is attained, and then the product is cooled under vacuum.

A 1% solution of the resulting product, prepared by stirring in cold water, shows a pH value of 4.9 and the following viscosities measured by a Brookfield-Viscosimeter at 20 r.p.m. and 25°C: 15 centipoises after one hour; 17.5 centipoises after 24 hours.

A 1% solution of the same product, after being heated for 10 minutes to 95°C and cooled to 25°C, shows the following vis-

cosities: 20 centipoises (C.P.) after 1 hour; 37 C.P. after 24 hours. A 3% solution of this product, after being heated for 10 minutes to 95°C and cooled to 25°C, shows a paste-like consistency and a viscosity of 6,300 C.P. This viscosity corresponds in order of magnitude to that (6,150 C.P.) of a 1% solution of the guar flour used as the starting material.

The degradation product of this example is valuable for use as a base for printing thickeners, particularly in the case of special fibers, such as acetate and nylon, in connection with which a higher amount of dry substance content is required. In small concentrations this product can be used advantageously for the production of surface-sized and coated papers in combination with starch derivatives.

EXAMPLE 5:

300 kg of pulverulent native caruba powder of commercial dryness is impregnated with 524g of HCl gas under vacuum and then is brought gradually to 105°C while maintaining a vacuum of 67 mm Hg absolute and stirring the mass in an autoclave. The material is thus subjected to a progressively increased removal of its water content. Thereafter the temperature is increased to 130°C while maintaining the vacuum, and the mass is subjected to continuous stirring under vacuum at this temperature for a period of approximately 2 hours until the desired degree of conversion is attained, whereupon cooling under vacuum follows.

A 1% solution of the resulting product, prepared by stirring in the cold, is practically colourless, has a pH value of 4.4 and the following viscosity measured by a Brookfield-Viscosimeter at 20 r.p.m. and 25°C: 12.5 C.P. after 1 hour; 15 C.P. after 24 hours.

A 1% solution of the same product, after being heated for 10 minutes to 95°C and cooled to 25°C, shows the following viscosities: 50 C.P. after 1 hour; 72 C.P. after 24 hours.

A 3% solution of the same product, after being heated for 10 minutes to 95°C and cooled to 25°C, shows a paste-like lardy consistency and a viscosity of 4,500 C.P. This value is somewhat lower than that (5,250 C.P.) of a 1% solution of the starting material.

The degradation product thus obtained is particularly valuable for use in various food products such as, for example, dessert products, soup products, ice creams, instant puddings, and instant sauces. It is also useful for stabilizing oil-water emulsions, thereby refining the aroma of the emulsions and giving them a desirable more mucous consistency.

As the material is degraded with the ex-

clusion of oxidizing media, the product is free from substances of undesired taste, such as aldehydes, and ketones, so it has wide ranges of usefulness in the foodstuff industry.

EXAMPLE 6:

20 kg of a mixture of guar flour which has been pretreated by fine grinding with 180 kg of potato starch is subjected to 10 vacuum in a stirring autoclave and then acidified with 50g of HCl gas. Subsequently the mixture is brought gradually during 3 hours to 110°C, while maintaining the vacuum, with continuous removal of water, 15 whereupon the temperature is raised to 150°C. These conditions are maintained during 1½ hours, whereafter the reaction mass is cooled under vacuum. A 10% solution of the end product which has been heated for 20 10 minutes to 95°C, shows a pH value of 3.3 and the following viscosities after cooling to 25°C, measured with a Brookfield-Viscosimeter, 20 r.p.m.: After 1 hour 150 C.P.; after 24 hours 140 C.P. The product 25 shows less tendency to retrogradation than pure potato starch degraded to an equal viscosity, yields more flexible films and is suitable for use as sizing agent, use in the manufacture and improvement of paper.

EXAMPLE 7:

A mixture of 80 kg of sugar flour of commercial dryness with 320 kg of native starch are mixed with 0.4 kg of polyoxymethylene. The mixture is subsequently acidified in an 35 autoclave provided with stirring means with 110 g of HCl gas under vacuum and gradually brought to 104°C during 2½ hours with continuous removal of water.

The temperature is then raised to 135°C, 40 while maintaining a vacuum of 57 mm Hg absolute and these conditions are maintained until the desired degree of conversion is attained, whereupon it is cooled under vacuum.

45 The resulting reaction product is distinguished by essentially decreased retrogradation, and by satisfactory film forming properties and is suitable especially as a base for printing thickeners in the textile industry.

WHAT WE CLAIM IS:—

1. A process for producing modification products of a natural substance of high molecular weight selected from the group consisting of galactomannans, polyuronic acids and galactans and mixtures thereof or 55 with other thermally degradable carbohydrate materials which comprises dehydrating a finely divided mass of said substance in its native form, or in a pretreated or

partially degraded form, if desired in presence of a reactant capable of degrading or forming a derivative with said substance, under vacuum at increasing temperatures insufficient to cause pasting in the mass, then while excluding oxygen from the mass treating it thermally or thermally and chemically until a desired degree of modification is attained, and then cooling the mass while excluding oxygen from it.

2. A process according to Claim 1, which comprises effecting the thermal or thermal and chemical treatment and the final cooling under vacuum.

3. A process according to Claim 1, which comprises effecting the thermal or thermal and chemical treatment and the final cooling in presence of a non-oxidizing gaseous medium.

4. A process according to Claim 1, which comprises effecting the thermal or thermal and chemical treatment and the final cooling in presence of an inert gaseous atmosphere.

5. A process according to Claim 1, which comprises effecting the thermal or thermal and chemical treatment and the final cooling in a reducing atmosphere.

6. A process according to Claim 1 or any of Claims 3 to 5, which comprises effecting the thermal or thermal and chemical treatment and the final cooling at atmospheric pressure.

7. A process according to any of the preceding claims in which the chemical treatment is an etherification, esterification, acetalization or incorporation of nitrogen.

8. A process according to Claim 1, which comprises dehydrating under vacuum at temperatures increasing into the range of 90 to 110°C a finely divided mass of substance containing free moisture until the mass practically ceases to release moisture, then heating the mass under continued vacuum to a higher temperature sufficient to degrade said substance thermally and heating the 100 mass at such higher temperature while excluding oxygen from it until a desired degree of modification of said substance is attained and then cooling the mass while excluding oxygen from it.

9. A process according to Claim 8, said higher temperature being in the range of 130 to 180°C.

10. A process for producing modification products of natural substances of high molecular weight selected from the group consisting of galactomannans, polyuronic acids and galactans substantially as described in any one of the examples hereinbefore described.

11. Thermal modification products of

natural substances selected from the group
consisting of galactomannans, polyuronic
acids and galactans, produced by a process
according to Claim 1 substantially as herein-
5 before described.

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